

ON

Paranitroorthotolylphenylsulphone

AND SOME OF ITS DERIVATIVES

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

—BY—

ROBERT STEWART NORRIS

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EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.
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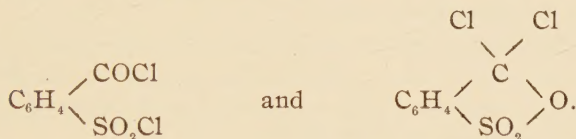
ACKNOWLEDGMENT.

This investigation was undertaken at the suggestion of Professor Ira Remsen, and carried out under his supervision. The author wishes to thank him for the advice and assistance received during the prosecution of the work involved and previous work, and also for instruction received in the lecture room, both of which have been a constant source of inspiration.

On Paranitroorthotolyphenylsulphone and Some of Its Derivatives.

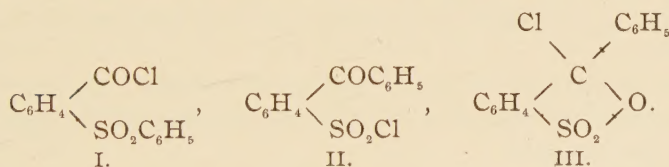
INTRODUCTION.

In a series of investigations carried on in this laboratory on derivatives of orthosulphobenzoic acid, it has been shown that when its potassium salt is treated with phosphorus pentachloride two isomeric chlorides are formed,¹ the formulas of which have been determined to be



On treating either of these chlorides with aluminum chloride and benzene, one of the chlorine atoms is replaced by a phenyl group; and the products formed are in both cases identical.² There must, therefore, be a rearrangement of the grouping of the atoms in one of the reactions.

There are three possible formulas for the product :



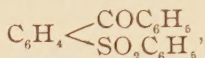
From its properties and reactions its most probable structure seems to be that represented by the second formula, the phenyl residue being in combination with a carbonyl group. Remsen and Saunders³ converted the chloride into the corresponding sulphonic acid by replacing the chlorine with a

¹ Remsen and Dohme : Am. Chem. J., **11**, 341; Remsen et al. : Am. Chem. J., **17**, 309; **18**, 791.

² Remsen and Saunders : Am. Chem. J., **17**, 360.

³ *Loc. cit.*

hydroxyl group, prepared a number of derivatives from this, and studied their properties. They also obtained a diphenyl derivative of orthosulphobenzoic acid of the formula



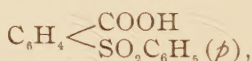
by the more prolonged action of benzene and aluminum chloride on the dichloride. The arguments which they bring forward in favor of the structure represented by the formula



for the first product of the action are :¹

1. That the acid formed by the decomposition of the chloride with water is a very soluble substance, and difficult to obtain in a crystalline form.

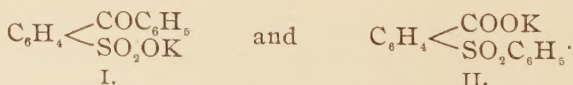
This is characteristic of sulphonic acids in general, while, on the other hand, the corresponding carboxylic acids are much less soluble, and are easily obtainable in the form of crystals. Paraphenylsulphonebenzoic acid,



for instance, described by Newell,² is a difficultly soluble, crystalline compound. Another example will be given later in this paper.

2. That the decomposition of the potassium salt by fusion with caustic potash gives benzoic acid and benzene sulphonic acid.

It is true that, on purely theoretical grounds, this might be a possible reaction with either of the substances represented by the formulas

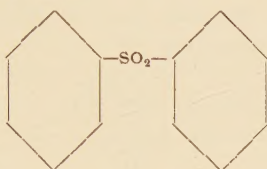


But when we come to consider the experimental evidence on the point it seems much more probable that these products would result from a compound having the first formula

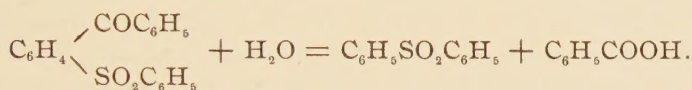
¹ Remsen and Saunders; *Loc. cit.*

² Inaug. Diss., Johns Hopkins University, 1895.

than one having the second. Diphenylsulphone, for instance, when fused with caustic potash, breaks down completely into diphenyl, sulphur dioxide, phenol, and various other substances.¹ Tolylsulphone acts in a similar manner.² And these reactions take place with difficulty, showing the stability of the sulphone grouping,



The way in which the diphenyl substitution product of orthosulphobenzoic acid breaks down also furnishes evidence in favor of this view. They found that it decomposes readily under similar circumstances into benzoic acid and diphenyl sulphone,



3. That the ethyl ether breaks down very readily into the acid on standing in contact with alcohol, which points to its being an ester of a sulphonic acid rather than of a carbonic acid.

4. That the chloride on treatment with ammonia, instead of forming an amide, goes into the lactim condition. This is in accordance with the supposition that the chlorine atom left in the molecule is the one united with the carbonyl group.

The evidence, therefore, seems pretty clear that of the two formulas,



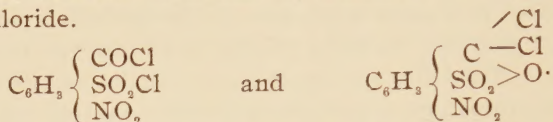
the former is the more probable for the compound obtained from the isomeric chlorides of orthosulphobenzoic acid by the Friedel and Crafts reaction with benzene.

Paranitroorthosulphobenzoic acid has also been found to

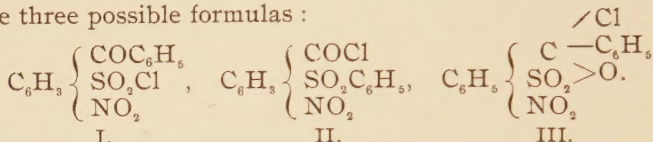
¹ Otto; Ber. d. chem. Ges., **19**, 2425.

² Otto; Loc. cit.

yield two isomeric chlorides¹ by treatment with phosphorus pentachloride.

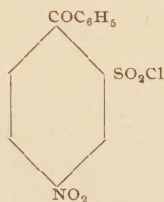


These in turn yield the same phenyl substitution-product when treated with benzene and aluminum chloride,² having the three possible formulas :



But the reaction seems in this case to stop here. No diphenyl substitution-product is formed by the further action of the reagents.

The same question arises in this case as in that of the compound just discussed : Which of the chlorine atoms is replaced by the phenyl group ? Hollis investigated the product formed and found from its properties and reactions somewhat similar evidence in favor of the first formula as that found by Remsen and Saunders³ in the former case. The acid obtained by decomposing the chloride with water was very soluble, and could not be obtained in the form of crystals. The ethyl ester of the acid, if one exists at all, is so unstable that it is immediately decomposed into the acid, when an attempt is made to prepare it from the chloride and absolute alcohol. On treating the chloride with ammonia an actim was formed. These three reactions are perfectly analogous to those which take place with orthobenzoylbenzenesulphone chloride, under similar conditions, and point to the structure



¹ Remsen and Gray : Am. Chem. J., **19**, 496.

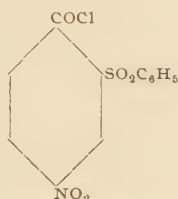
² Hollis: Inaug. Diss., Johns Hopkins University, 1896.

³ *Loc. cit.*

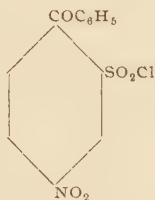
for the chloride. But the most conclusive evidence obtained by Remsen and Saunders for the formula which they gave, namely, the formation of certain products by fusing the acid with caustic potash, was not duplicated in the present case. The presence of the nitro group would probably make such a test less satisfactory. The evidence in this case, therefore, is not as strong as it is in that of the more simple compound.

There is, however, another method of attacking the problem by which just as conclusive evidence, but of a different kind, might be obtained. It was for the purpose of determining the nature of this evidence that the present investigation was undertaken.

If a compound having the formula :



could be prepared, and its properties should be different from the compound obtained by Hollis from the isomeric chlorides of paranitroorthosulphobenzoic acid, the latter could not have the same structure, and, therefore, would probably have the formula :



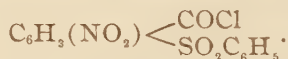
If the properties should be the same, the structure of the two would, of course, be identical.

METHOD.

The best method which suggested itself for preparing paranitroorthophenylsulphonecarbonyl chloride was to start with paranitrotoluene, convert it into paranitroorthotoluenesul-

phonic acid by treatment with fuming sulphuric acid, treat the potassium salt of this with phosphorus pentachloride to form paranitroorthotoluenesulphone chloride, from which paranitroorthotoluenephynylsulphone could be made by the Friedel and Crafts reaction with benzene. By oxidation of the methyl group in this sulphone, paranitroorthophenylsulphonebenzoic acid would be formed, and this could be transformed into paranitroorthophenylsulphonebenzoyl chloride by the action of phosphorus pentachloride.

Another method which was suggested was to convert paranitrocyanbenzeneorthosulphonic acid, $\text{C}_6\text{H}_3(\text{NO}_2) < \begin{smallmatrix} \text{CN} \\ \text{SO}_3\text{H} \end{smallmatrix} (o)$ into its chloride, $\text{C}_6\text{H}_3(\text{NO}_2) < \begin{smallmatrix} \text{CN} \\ \text{SO}_2\text{Cl} \end{smallmatrix}$, replace the chlorine with phenyl, hydrolyze the cyan group into a carboxyl group, $\text{C}_6\text{H}_3(\text{NO}_2) < \begin{smallmatrix} \text{COOH} \\ \text{SO}_2\text{C}_6\text{H}_5 \end{smallmatrix}$, and treat with phosphorus pentachloride to form paranitroorthophenylsulphonebenzoyl chloride,



Positive results were not obtained by this method.

PREPARATION OF MATERIAL.

Paranitroorthotoluenesulphonic Acid.

This acid was prepared by the method originally described by Beilstein and Kuhlberg,¹ and later used by Hart, Kastle, Gray, and others,² in this laboratory. There are a number of important details not mentioned in any one article, that it is necessary to observe in order to obtain a good yield and a pure product, so it may not be out of place to give the details of the process by which these results were attained.

Four hundred grams of pure paranitrotoluene were placed in a three liter flask, and sixteen hundred grams of fuming sulphuric acid added. The fuming sulphuric acid contained in the original sealed bottles is sufficiently strong for the purpose, but acid which has been standing for any length of time in the bottles after they have once been opened, has usually ab-

¹ Ann. Chem. (Liebig), **155**, 8.

² Inaug. Dissertations, Johns Hopkins University.

sorbed so much water as to be unfit for use in this preparation. The addition of sulphur trioxide to the acid before using is to be recommended in the latter case.

The flask was placed on a large water-bath so as to be immersed in the water up to the neck, and the water heated to boiling. At intervals of fifteen to twenty minutes the solution was thoroughly agitated by shaking the flask. After the solution had been heated for two or three hours, a sample was occasionally removed from the flask and added to water to determine when the action was completed, which was indicated by the formation of a clear solution. The time taken to completely sulphurize the nitrotoluene depends mainly on the strength of the acid. In the present case it took eight hours. At the end of that time the solution was allowed to cool down to the ordinary temperature. The dark brown syrupy liquid obtained in this manner was poured into about sixteen liters of water, contained in large evaporating dishes, which were not more than two-thirds full. If the reaction has taken place properly, the thoroughly mixed water solution should be quite clear and free from any undissolved matter. Should this not be the case, the solution is filtered. Calcium carbonate—precipitated chalk—was then added in small portions to the acid solution until no further effervescence took place, the solution being stirred during the addition. The precipitated calcium sulphate and excess of calcium carbonate were filtered off through a cloth filter. This did not remove all of the precipitate, so it was necessary to filter again through paper, in order to prevent the formation of a large amount of soluble potassium sulphate in the next stage of the process. The collected calcium sulphate precipitates were extracted with water, and the supernatant liquid decanted off through a filter, and added to the main solution, which was then heated to boiling. A solution of potassium carbonate was added until litmus paper indicated a slight alkalinity, and the precipitated calcium carbonate filtered off. The dark brown solution was boiled for an hour with animal charcoal, and again filtered. The removal of the animal charcoal was found to be a slow process, and best accomplished by means of a large fluted filter paper. The use of the filter-pump

with a flat filter did not hasten the process. A Witt plate covered with a small filter paper, used in connection with the filter-pump, and previous filtration through cloth, were tried, but with little success. The charcoal did not remove all of the color from the solution, which was still brownish yellow. It was evaporated to one-half of its original volume, and the potassium salt allowed to crystallize out over night. The solution filtered off from the first crop of crystals was further concentrated, more potassium salt crystallized out, and so on, until the volume of the solution became equal to about two liters, when it was again treated with animal charcoal, filtered, and evaporated down to one liter. The mother-liquor left after the crystals had separated out of this solution, was thrown away, and the crystals formed recrystallized from water. The crystals which separated out at different times were drained as thoroughly as possible with the filter-pump, spread out on large sheets of drying paper of double thickness, which were changed occasionally for dry sheets, and left until thoroughly dry. In this condition they appeared as very light yellow needles. Six hundred and twenty-two grams of the dry salt were obtained from the four hundred grams of paranitrotoluene used.

It has been shown by Ascher¹ that the compound formed by the action of fuming sulphuric acid on paranitrotoluene is paranitroorthotoluenesulphonic acid. He converted the acid

formed by this reaction, $C_6H_3 \left\{ \begin{array}{l} CH_3 \\ SO_3H \\ NO_2 \end{array} \right.$, into amidotoluenesul-

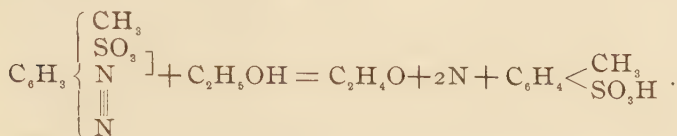
phonic acid, $C_6H_3 \left\{ \begin{array}{l} CH_3 \\ SO_3H \\ NH_2 \end{array} \right.$, by reduction of the nitro group,

which is known to be in the para position with reference to the methyl group, on account of the formation of the acid from paranitrotoluene. This was diazotized to paradiazo-

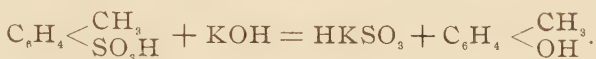
toluenesulphonic acid, $C_6H_3 \left\{ \begin{array}{l} CH_3 \\ SO_3H \\ N \\ ||| \\ N \end{array} \right.$, which was converted into

¹ Ann. Chem. (Liebig), 161 7.

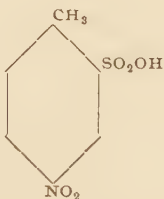
toluenesulphonic acid by boiling with absolute alcohol, according to the following reaction :



On fusing this product with caustic potash, a reaction which may be represented by two equations took place :



And the product formed was found to be the potassium salt of salicylic acid, $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{COOK} \\ \text{OH} \end{array} \right.$ (1). Therefore the nitrotoluenesulphonic acid started from must have had the structural formula,



and the product obtained by the process above described is the potassium salt of paranitroorthotoluenesulphonic acid.

Paranitroorthotoluenesulphone Chloride.

Jensen¹ heated the potassium salt of paranitroorthotoluenesulphonic acid to 190° C., and found that it did not lose in weight. It is therefore unnecessary to heat the salt before treating it with phosphorus pentachloride. The method made use of in preparing the chloride was that first used by Jensen². 460 grams of the potassium salt of paranitroorthotoluenesulphonic acid were treated in twenty gram portions with an equal weight of phosphorus pentachloride, thoroughly mixed in a mortar and

¹ Ann. Chem. (Liebig), 172, 230.

² Loc. cit.

placed in a small evaporating dish on a sulphuric acid bath. The bath was heated up, and reaction began when the temperature reached 120° – 130° C., continuing at the same temperature until completed. The semi-liquid mass was kept at this temperature for half an hour, in order to evaporate the phosphorus oxychloride. After allowing it to cool to the ordinary temperature, it was poured into a tall cylinder containing water at 60° – 70° C., and agitated with the water by means of a copper disk on the end of a glass rod. The warm water keeps the chloride in a liquid state, in which condition it can be more thoroughly washed than when in a solid form. After allowing the chloride to settle, the wash-water was decanted or siphoned off, more warm water added and the process of washing repeated. Cold water was finally added, upon being shaken up with which the chloride immediately solidified. It was ground in a mortar to a fine powder and washed with cold water until the wash-water, which was decanted off through a filter, was free from phosphoric acid. The water was drained off by means of a filter-pump, and the chloride dried with drying paper. 370 grams were obtained.

The paranitroorthotoluenesulphone chloride prepared in this way was a yellow powder, melting at 43° – 45° C., and readily soluble in ether, from which it crystallized in large, rhombic crystals, melting at 44° C. (uncor.).

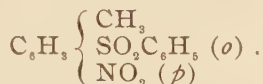
Although a number of different methods were tried, none were found to yield as good results as this one. Too high a temperature, or heating too long, decreases the yield, and makes the chloride dark. The purity of the product depends a great deal on that of the potassium salt used. The color of the latter was found to be carried over into the chloride.

Paranitroorthotoluenesulphone chloride has been described as a liquid.¹ The sharp melting-point of the product obtained by the above process, and crystallized from ether, is conclusive evidence of its purity; and the existence of the chloride in the liquid state at the ordinary temperature must be ascribed to the presence of some impurity. It is a common experience in working with solid sulphone chlorides, that the

¹ Noyes : Am. Chem. J., 8, 167.

ease with which any particular specimen can be made to crystallize is very much dependent on its purity.

PARANITROORTHOTOLYLPHENYLSULPHONE,



This was obtained from the chloride just described, by means of the Friedel and Crafts reaction with benzene.

Limpricht¹ obtained a compound isomeric with this, by the action of aluminum chloride and toluene on metanitrobenzenesulphone chloride,



the nitro and methyl groups being attached to different benzene rings. From the properties which are given, it seems to be quite different from paranitroorthotolylphenylsulphone, except in solubility. One of these points of difference will be taken up later under the subject of the action of oxidizing agents on the sulphone.

Preparation and Properties.

As a preliminary experiment, ten grams of the chloride were dissolved in about 100 cc. of benzene, in a small flask provided with a condensing-tube. About four grams of aluminum chloride, in small pieces, were added, and the solution warmed gently. Action began slowly with the evolution of hydrochloric acid from the surface of the aluminum chloride. The solution began to darken quickly, so after heating for five minutes, the action was stopped by cooling the flask, and the contents were poured into half a liter of cold water containing 20 cc. of concentrated hydrochloric acid. The benzene solution was then separated from the water and evaporated to dryness. The residue left—a dark brown, tarry mass—was treated in different portions with alcohol, ether, chloroform, and benzene, and the solutions filtered. Crystals separated from each of the solutions

¹ Ann. Chem. (Liebig), 278, 257.

on evaporation, but the ether and alcohol dissolved less of the dark tarry substance, and consequently furnished the best crystals.

It was found on further experimenting that the aluminum chloride reacted more satisfactorily when powdered, and that it was not necessary to use such a large proportion of benzene. The darkening which takes place rapidly after the action begins could not be prevented, and it was found to have less effect on the final product than was at first supposed.

Previously to using the method finally adopted the yield was small, only 6 grams of the sulphone being obtained from 35 grams of the chloride. This method is similar to that used by Beckurts and Otto¹ in preparing paratolyl-phenylsulphone from benzenesulphone chloride and toluene, and by Newell² in making the same substance from paratoluenesulphone chloride and benzene. Only 20 grams of the chloride were used at a time, as this was found to be the most convenient amount to handle. It was dissolved in an equal weight of warm benzene in a flask connected with a condensing tube. The solution was placed on a water-bath, and heated so that the benzene solution boiled gently. Fifteen grams of powdered aluminum chloride were added gradually 3 or 4 grams at a time—allowing the violent action to subside after each addition. The solution was heated for half an hour, allowed to cool, poured into a litre of water containing 20–30 cc. of concentrated hydrochloric acid. A voluminous light brown flocculent precipitate formed. The solution was warmed on the water-bath until all of the benzene had evaporated, the precipitate filtered off, and drained with the filter-pump. This process was repeated until 200 grams of the chloride had been used. Most of the precipitate was found to be soluble in alcohol, but the yield was considerably decreased in the process of purification.

The collected residues were extracted with hot alcohol, and the alcoholic solution boiled with animal charcoal until nearly colorless, and filtered while hot with the use of a hot-water

¹ Ber. d. chem. Ges., II, 2068.

² Inaug. Diss., Johns Hopkins University, 1895.

funnel. The marked difference in the solubility of the sulphone in hot and cold alcohol caused considerable difficulty in its purification. Most of it crystallized out from the alcohol on cooling, in the form of thin, silver-white plates, melting at 158°C . (uncor.). That which remained dissolved in the cold alcohol was obtained by concentrating the solution. This part of the product was not as pure as that which separated out from the original solution, as it was found that an alcoholic solution of the sulphone became brown when boiled for a while, or even allowed to stand at the ordinary temperature for more than a day. The charcoal took up a considerable amount of the sulphone, which was recovered by extracting with alcohol.

Analysis of the product gave the following results :

I. 0.3140 gram gave 0.2652 gram BaSO_4 .

II. 0.1583 gram gave 0.1356 gram BaSO_4 .

III. 0.2863 gram gave 0.5934 gram CO_2 and 0.1058 gram H_2O .

IV. 0.2994 gram gave 0.6201 gram CO_2 and 0.1053 gram H_2O .

V. 0.3229 gram gave 0.017 gram N.

	Calculated for $\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS}^1$	I.	II.	Found. III.	IV.	V.
C	56.30			56.56	56.52	
H	4.00			4.13	3.93	
S	11.56	11.60	11.76			
N	5.06					5.26

Paranitroorthotolylphenylsulphone exhibits in a marked degree the general stability of sulphones toward concentrated acids. It is, however, much less stable toward alkalies than the simpler sulphones, probably on account of the presence of the nitro group. Most of the ordinary organic solvents dissolve it easily.

It was found to be nearly as soluble in methyl alcohol as in ethyl alcohol. Benzene and acetone dissolved it very readily, and it crystallized out from both in plates, which, in the latter case, were very narrow and had the appearance of needles to the naked eye. It was almost equally soluble in hot and

¹ All calculations in this paper are made on the basis of the atomic weights tabulated by Clarke : J. Am. Chem. Soc., 19, 368.

cold ether, and to rather a small extent. Hot ligroin dissolved it with ease. In water it is practically insoluble, even in boiling water; but that it does dissolve to a limited extent is shown by the fact that the filtrate from a water solution gives a faint yellow color when boiled with caustic potash solution. This is a very delicate test, as one small crystal of the sulphone, dissolved in alcohol, gives a distinct red color with caustic potash solution.

Dilute nitric and sulphuric acids dissolve the sulphone in small amounts; dilute hydrochloric acid does not dissolve it. Concentrated nitric and sulphuric acids were found to dissolve it quite appreciably in the cold, and to give it up again on dilution with water. A small amount was boiled with concentrated nitric acid for five minutes, the solution cooled, and diluted with water. The sulphone was precipitated in crystalline form, and it melted sharply at 158°C. , showing that it had not been acted upon by the acid. A similar experiment was tried with fuming nitric acid, with the same result. A mixture of equal parts by volume of concentrated nitric and sulphuric acids was then tried; the sulphone which crystallized out on dilution had a sharp melting-point. When boiled with a mixture of concentrated sulphuric and fuming nitric acids it was slightly decomposed. There was no apparent action, but the white precipitate which formed on dilution did not melt sharply.

The sulphone dissolved quite readily in ordinary concentrated sulphuric acid in the cold, and was precipitated unchanged when the solution was poured into water. When the acid was warmed to 100°C. the solubility of the sulphone increased, but it was not acted upon. When the temperature was raised much above this the sulphone was decomposed, as shown by the charring. Fuming sulphuric acid dissolved the sulphone easily, and it was not precipitated on dilution.

Action of Fuming Sulphuric Acid.

A small amount of the sulphone was treated with fuming sulphuric acid in a test-tube, and heated gently for four or five minutes, not higher than 100°C. After cooling, the

solution was poured into a small amount of water. A precipitate formed, but on the addition of more water, it redissolved, and did not reappear on further dilution. The precipitate could not, therefore, have been the sulphone, nor could the solution have contained any of it, as it would have been precipitated on diluting. The sulphone had been completely converted into a more soluble substance.

The experiment was repeated on a larger scale. Ten grams of the sulphone were treated with about 40 grams of fuming sulphuric acid, and heated on a water-bath to 100°C . for half an hour, then allowed to cool, and poured into half a liter of water. No precipitate formed. Barium carbonate was added to the solution till it no longer caused effervescence. After boiling, the barium sulphate and excess of barium carbonate were filtered off. During the digestion of the sulphone with acid, the solution became dark brown, and the color increased in intensity during the heating. This color appeared again in the barium salt, so it was necessary to treat it with animal charcoal. After this the solution was allowed to cool, and the barium salt crystallized out as white needles.

Analysis gave the following results:

0.0849 gram lost 0.0097 gram at 150°C ., and gave 0.0209 gram BaSO_4 .

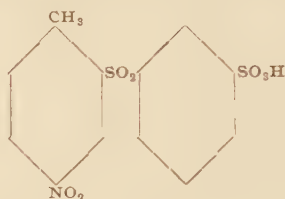
	Calculated for ($\text{C}_{13}\text{H}_{10}\text{O}_7\text{S}_2\text{N}$) ₂ Ba+6H ₂ O.	Calculated for ($\text{C}_{13}\text{H}_{10}\text{O}_7\text{S}_2\text{N}$) ₂ Ba.	Found.
H ₂ O	11.28		11.42
Ba		16.16	16.35

Paranitroorthotolylphenylsulphonesulphonic Acid.—This acid was obtained from the barium salt by treating a solution of the latter with just sufficient sulphuric acid to precipitate the barium as barium sulphate, and filtering. It was found to be readily soluble in water, and crystallized from the solution in the form of very fine white needles. They were readily soluble in acetone, but difficultly in ether and benzene.

From analogy to the sulphonic acid formed from phenylsulphone,¹ and from the fact that three of the positions in one of the benzene rings already contain substituted groups, it seems probable that the sulphonic acid residue enters the

¹ Otto and Knoll: Ber. d. chem. Ges., 11, 2075; Otto: Ber. d. chem. Ges., 19, 2417.

phenyl group of the sulphone in the meta position, giving a compound of the formula,



Action of Potassium Hydrate.

A mere trace of the sulphone in solution gives a purplish-red color with caustic potash.

A few crystals of the sulphone were dissolved in alcohol and the solution of caustic potash added. Upon being heated the solution quickly assumed a deep purple color, which became more red after boiling for awhile, and finally a purplish red precipitate formed. Dilute hydrochloric, nitric, and sulphuric acids were added to different portions of the solution. They changed the color to reddish yellow, and the purple color was restored on addition of excess of potassium hydrate. The purple color was not brought back, however, with either ammonium hydrate or sodium carbonate. Concentrated sulphuric, nitric, and hydrochloric acids each produced apparently the same result as the dilute acids. But when the solutions were made alkaline again with caustic potash, the purple color did not return. The purple-colored compound was evidently decomposed by the concentrated acids.

Caustic soda had the same effect on the sulphone as caustic potash. Ammonium hydrate and sodium carbonate had no action on the sulphone.

An attempt was made to isolate the compound formed. About five grams of the sulphone were dissolved in absolute alcohol, and treated with an alcoholic solution of pure potassium hydrate. The solution was boiled for five minutes, cooled and poured into about a liter of water. A red flocculent precipitate settled to the bottom of the vessel, leaving the supernatant liquid clear and not very deeply colored. The precipitate was washed by decantation until no longer alka-

line, then boiled with water and washed again. After filtering off and drying, its solubility in a number of solvents was tried for the purpose of finding a method for purifying it. Treated with alcohol, ether, acetone, and acetic acid, it gave a slight red color to each, but did not dissolve appreciably. Evaporation of the solutions in each case left but a trace of amorphous residue. Concentrated sulphuric acid dissolves it to a certain extent, forming a deep purple-colored solution. On diluting, the color changed to reddish yellow, and the original purple color did not appear again on making the solution alkaline with potassium hydrate. The substance left quite a large amount of ash on being ignited, consisting evidently of the potassium hydrate that could not be removed by washing. On account of its insolubility the substance could not be obtained pure.

Action of Reducing Agents.—Ammonium Sulphide.

Gericke¹ found that when nitrophenylsulphone in alcoholic solution was treated with ammonium sulphide and heated, it was reduced to amidophenylsulphone. Noyes² has shown also that paranitroorthosulphobenzoic acid is easily reduced by the same reagent to paramidoorthosulphobenzoic acid.

The nitro group of paranitroorthotolylphenylsulphone was also found to be readily converted into an imido group in the same way.



Four grams of paranitroorthotolylphenylsulphone were dissolved in 100 cc. of hot alcohol, about 20 cc. of concentrated ammonia water added, and sulphuretted hydrogen passed into the solution for fifteen minutes. The solution became blood-red in a short while, and increased in temperature. At the end of this time no sulphone could be made to crystallize out of the solution on cooling, whereas it came out of the original solution easily on a slight lowering of the temperature. A small amount of the solution was removed and treated with water, which caused a voluminous precipitate of short, needle-

¹ Ann. Chem. (Liebig), 100, 208.

² Am. Chem. J., 8, 167.

shaped crystals to form. The main portion of the solution was then evaporated to dryness on a water-bath, and the residue digested with water containing a small amount of hydrochloric acid. The portion remaining undissolved, which consisted of sulphur, was removed by filtration through a layer of flowers of sulphur in a Gooch crucible. On making the filtrate alkaline with caustic soda, a heavy white precipitate came down. This was filtered off, washed, and drained with the filter-pump. It was then dissolved in alcohol, treated with animal charcoal, boiled, filtered, and allowed to crystallize out. The crystals were large, thin, irregular shaped, colorless plates, and melted at 156°C . (uncor.). They were difficultly soluble in hot water, and crystallized out from this solution in very small plates. Alcohol and acetone dissolved them readily, and they were not precipitated from either solution on addition of water. They dissolved to only a small extent in either cold or boiling ether. Benzene dissolved them very readily, and the compound crystallized out in the form of needles.

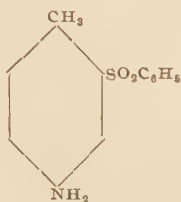
Determination of nitrogen gave the following results :

I. 0.1681 gram gave 8 cc. N at 19°C ., and 765 mm. Hg. pressure = 0.009264 gram.

II. 0.3496 gram gave 17.5 cc. N at 20°C ., and 755 mm. Hg. pressure = 0.0199 gram.

	Calculated for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{NS}$.	I.	Found.	II.
N	5.67	5.51		5.69

From its formula,



it will be seen that this compound is a derivative of paratoluidine, and as such it forms salts with acids. Use is made of the easy solubility of the hydrochloride in separating the sulphone from sulphur in the above process.

Action of Oxidizing Agents.

1. *Chromic Acid*.—Newell¹ found that the best method for converting paratolylphenylsulphone into paraphenylsulphone-benzoic acid, was by treatment with chromic acid in glacial acid solution. The same method was tried with this sulphone.

Ten grams of the sulphone were dissolved in glacial acetic acid and heated to boiling in a flask provided with a return condenser. A saturated solution of about 12 grams of chromic acid in glacial acetic acid was added, in small quantities at a time, the solution being kept just hot enough to boil gently. After all the chromic acid had been added, the solution was boiled for three hours. It was filtered, and the acetic acid evaporated off from the filtrate. The original precipitate was found to consist of chromic oxide, Cr_2O_3 , almost free from organic matter. The residue from the filtrate consisted principally of unaltered sulphone mixed with the chromic acid that remained.

A repetition of the experiment gave the same result.

The action of chromic acid in this case, or rather its lack of action, is in accord with its usual behavior toward ortho-substitution products of toluene. The presence of the phenylsulphone group, $\text{SO}_2\text{C}_6\text{H}_5$, in the ortho position to the methyl group, seems to shield the latter from the action of chromic acid.

2. *Potassium Permanganate*.—The most efficient oxidizing agent for the ortho-substitution toluenes has generally been found to be potassium permanganate in water solution.

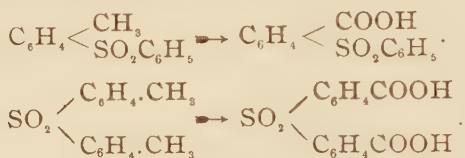
The action of oxidizing agents on sulphones was first investigated by R. Otto. He found² that when phenyl sulphone, mixed with water acidified with sulphuric acid, was treated with potassium permanganate, the permanganate was somewhat reduced, as shown by the precipitation of manganese dioxide. Michael and Adair³ showed later that tolylphenylsulphone and ditolylsulphone were oxidized by potassium

¹ *Loc. cit.*

² *Ann. Chem. (Liebig)*, **145**, 37.

³ *Ber. d. chem. Ges.*, **11**, 119.

permanganate to a phenylsulphonebenzoic acid and a phenylsulphonedibenzoic acid respectively,

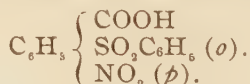


When the reaction was carried on in acetic acid solution the yield was small. A water solution of potassium permanganate gave much better results, although the sulphone was but little soluble in water, and only half of it was oxidized by the theoretical quantity of potassium permanganate.

Paranitroorthotolylphenylsulphone was found to act in a similar manner.

Morawski and Stingl¹ have determined by experiment that one molecule of potassium permanganate, KMnO_4 , gives up one and a half atoms of its oxygen to an oxidizable substance when no free mineral acid is present. It would therefore require two molecules of the permanganate to one of the sulphone, if all of the oxygen liberated was used in oxidizing methyl to carboxyl. It was found, however, that a much larger quantity was required. This is to be accounted for partly by the fact that the sulphone is probably completely broken down, to a small extent, into higher oxidation products,² and also that the manganese dioxide first formed decomposed some of the potassium permanganate³ still present.

PARANITROORTHOPHENYLSULPHONEBENZOIC ACID,



The acid was prepared by the following method :

Ten grams of the sulphone were suspended in a liter of water in a one and a half liter flask. The sulphone had previously been powdered as fine as possible in a mortar. A solution of thirty grams of potassium permanganate was added,

¹ J. prakt. Chem. **126**, 78.

² R. Otto : *Loc. cit.*

³ Morse, Hopkins and Walker : Am. Chem. J., **18**, 401 ; Morse : Ber. d. chem. Ges. **30**, 48.

one-quarter at a time, at intervals of an hour, to the solution which was heated to boiling meanwhile on a sand-bath. The color of the permanganate was gradually displaced by that of the manganese dioxide, as the reaction progressed. It was difficult to determine, from the appearance of the solution, when the last traces of the permanganate had disappeared, without letting the solution settle, which required considerable time. A small amount of the solution was removed occasionally and filtered, and when a colorless filtrate was obtained the heating was stopped. It usually required eight hours to decompose all of the potassium permanganate. The solution was allowed to cool, and filtered. On acidifying the filtrate with hydrochloric acid a finely divided, white precipitate came down, and on standing it aggregated into irregular, needle-shaped crystals. It was filtered off and purified by redissolving in water, and treating with animal charcoal. The largest yield obtained at one time was 2.8 grams of the acid from 10 grams of the sulphone. A considerable amount of sulphone was always left unacted upon, and mixed with the manganese dioxide precipitate. It was recovered by dissolving the dioxide in concentrated hydrochloric acid and filtering off the undissolved sulphone, which was not attacked by the nascent chlorine. Otto¹ found that phenylsulphone also is not attacked by nascent chlorine in solution, but on the other hand that dry chlorine acts on the sulphone at its melting point to form benzenesulphone chloride and monochlorbenzene.²

Paranitroorthophenylsulphonebenzoic acid crystallizes in white needles 5 to 10 mm. long, melting at 196° C. (uncor.) It is difficultly soluble in cold water, and not very readily in hot water. It has a bitter-sweet taste. Acetone dissolves it readily, but ether and benzene only to a small extent.

Salts of Paranitroorthophenylsulphonebenzoic Acid.

Barium Nitrophenylsulphonbenzoate, $(C_6H_4NO_2SO_2C_6H_4COO)_2Ba.H_2O$, was obtained by dissolving barium carbonate in a solution of the acid. It crystallizes in the form of

¹ R. Otto : *Loc. cit.*

² Ann. Chem. (Liebig), 141, 93.

short, white needles, matted together, and difficultly soluble in hot water. Analysis gave the following results :

I. 0.3784 gram lost 0.0100 gram at 178° C., and gave 0.1146 gram BaSO_4 .

II. 0.5043 gram lost 0.0125 gram at 178° C., and gave 0.1524 gram BaSO_4 .

	Calculated for ($\text{C}_{13}\text{H}_8\text{O}_6\text{NS}$) $_2$ $\text{Ba}\cdot\text{H}_2\text{O}$.	Calculated for ($\text{C}_{13}\text{H}_8\text{O}_6\text{NS}$) $_2$ Ba .	Found. I.	Found. II.
H_2O	2.34		2.64	2.48
Ba		18.32	18.30	18.23

Calcium Nitrophenylsulphonebenzoate, ($\text{C}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_5\text{COO}$) $_2$ $\text{Ca}\cdot 6\frac{1}{2}\text{H}_2\text{O}$, was obtained by boiling a solution of the acid with an excess of powdered calcite. It crystallizes in tufts of radiating, colorless, prismatic crystals, easily soluble in hot water. Analysis of the salt gave the following results :

0.1907 gram lost 0.0292 gram at 160° C., and gave 0.0342 gram CaSO_4 .

	Calculated for ($\text{C}_{13}\text{H}_8\text{O}_6\text{NS}$) $_2$ $\text{Ca}\cdot 6\frac{1}{2}\text{H}_2\text{O}$.	Calculated for ($\text{C}_{13}\text{H}_8\text{O}_6\text{NS}$) $_2$ Ca .	Found.
H_2O	15.21		15.31
Ca		6.14	6.23

Comparison of Paranitroorthophenylsulphonebenzoic Acid with Paranitroorthobenzoylbenzenesulphonic Acid.

Hollis¹ found that the acid formed by the action of water and dilute acids on the product of the Friedel and Crafts reaction with the chlorides of paranitroorthosulphobenzoic acid, was very easily soluble in water, and could not be obtained in a crystallized form. Its barium salt crystallized with varying amounts of water of crystallization, but with never less than three molecules. The crystals had the form of tufts of radiating needles or monoclinic prisms. Its calcium salt crystallized in thin plates with three molecules of water of crystallization.

Paranitroorthophenylsulphonebenzoic acid, on the other hand, is rather difficultly soluble in water, and crystallizes easily. Its barium salt crystallizes as short needles, matted together, and containing one molecule of water of crystallization. And its calcium salt crystallizes in prisms containing six and a half molecules of water of crystallization.

¹ *Loc. cit.*

The difference can be brought out more strikingly by means of the following table :

Table.

Paranitroorthobenzoylbenzenesulphonic Acid.

Very soluble in water.

Not crystallizable.

Barium salt contains from three to seven molecules of water of crystallization, and crystallizes in tufts of radiating needles or monoclinic prisms.

Calcium salt crystallizes in plates with three molecules of water of crystallization.

Paranitroorthophenylsulphonebenzoic Acid.

Difficultly soluble in water.

Crystallizes easily.

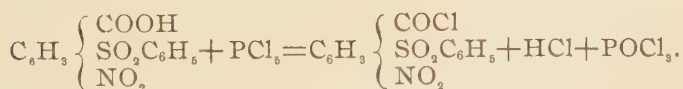
Barium salt contains one molecule of water of crystallization, and crystallizes in short, matted needles.

Calcium salt crystallizes in prisms with six and a half molecules of water of crystallization.

Action of Phosphorus Pentachloride on Paranitroorthophenylsulphonebenzoic Acid.

Phosphorus pentachloride acts readily on the free acid, to form paranitroorthophenylsulphonebenzoyl chloride.

When the acid was intimately mixed with phosphorus pentachloride, free from oxychloride, no action was noticed until the temperature was raised to 160° C. But when the pentachloride contained phosphorus oxychloride, the reaction began immediately at the ordinary temperature on mixing the two together. The reaction which takes place may be represented thus :



PARANITROORTHOPHENYLSULPHONEBENZOYL CHLORIDE.

Equal weights of paranitroorthophenylsulphonebenzoic acid and phosphorus pentachloride containing a small amount of the oxychloride were intimately mixed in a mortar. The mixture gradually softened into a semi-liquid mass, with rise of temperature, and liberation of hydrochloric acid and phos-

phorus oxychloride. After the action was over the mass was transferred to an evaporating dish and heated about ten minutes longer at about 150°C . It then had the appearance of a light brown transparent liquid. It was allowed to cool to the ordinary temperature, and washed with cold water, which caused it to solidify to a light yellow granular solid. It was reduced to a fine powder and washed until free from phosphoric acid, dried with drying-paper, and dissolved in warm chloroform. It crystallized out of the solution on the spontaneous evaporation of the chloroform, as well-formed, colorless, rhombic crystals, from one to five millimeters long, having a melting-point of 109°C . (uncor.). The crystals were easily soluble in chloroform, ether, benzene and ligroin.

The chlorine in the chloride was determined by boiling with a dilute solution of pure caustic soda (made from metallic sodium), acidifying with nitric acid and precipitating with silver nitrate.

I. 0.1631 gram gave 0.0716 gram AgCl .

II. 0.1847 gram gave 0.0810 gram AgCl .

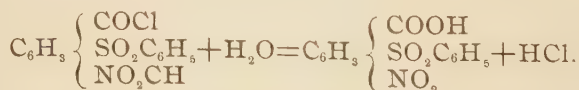
	Calculated for $\text{C}_{13}\text{H}_8\text{O}_6\text{NSCl}$.	I.	Found.	II.
Cl	10.88	10.85		10.84

Action of Water.

The chloride is quite stable in the presence of water at ordinary temperatures. No change could be detected in crystals which remained in contact with water several days. But it is readily decomposed when boiled with water.

Dilute caustic alkalies in solution decompose the chloride much more quickly than water. Two-tenths of a gram of the chloride was entirely decomposed when boiled with a very dilute solution of caustic potash for five minutes. Hydrochloric acid was added in excess to the solution, and very fine needle-shaped crystals separated out on cooling. Their melting-point, 196°C ., showed them to be paranitroorthophenylsulphonebenzoic acid.

The reaction may be represented thus :



Action of Ammonia.

By the action of ammonia the chlorine of the carbonyl chloride group is replaced by an amido residue.

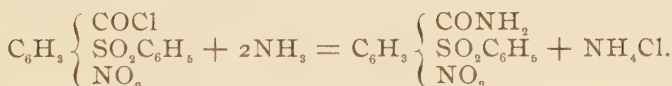
Some of the finely powdered chloride was added to a dilute solution of ammonia in a flask and allowed to remain in contact with it for several days. The solid material in the bottom of the flask at the end of this time had the same appearance as the chloride—a light yellow powder. The ammonia was evaporated off on a water-bath, and the solution filtered from the residue, which was washed, dried, and dissolved in hot chloroform, in which it was not very readily soluble. It crystallized out on spontaneous evaporation of the chloroform in well-formed, colorless, prismatic crystals, apparently monoclinic, and melting at 191° - 192° C. (uncor.). The crystals were analyzed with the following results:

I. 0.4049 gram gave 0.3004 gram BaSO_4 .

II. 0.1515 gram gave 0.01385 gram N.

	Calculated for $\text{C}_{18}\text{H}_{16}\text{O}_6\text{N}_2\text{S}$.	I.	Found.
			II.
S	10.46	10.19	
N	9.16		9.14

The reaction which takes place, therefore, is,



The result being the formation of

Paranitroorthophenylsulphonebenzamide.—The amide is practically insoluble in water, benzene, and ether. It dissolves readily in hot alcohol, and crystallizes out as the solution cools, in the form of prisms. Acetone also dissolves it very easily, and well-formed prisms crystallize out on evaporation of the acetone.

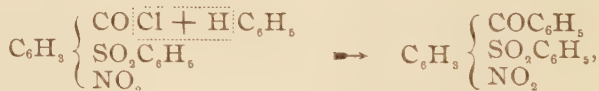
Action of Benzene and Aluminum Chloride.

On adding aluminum chloride to a warm solution of the orthosulphonebenzoyl chloride in benzene, a slight evolution of hydrochloric acid took place, and a brown, tarry mass, which was insoluble in the benzene, very soon collected around the aluminum chloride and prevented further action.

Two grams of the chloride were dissolved in about ten grams of benzene, and two grams of powdered aluminum chloride added. The solution was heated on a water-bath until it just began to boil, and kept at this temperature. Hydrochloric acid was given off quite rapidly at first, passing out in a continuous stream from the condensing-tube. After the evolution of acid had ceased, the solution was cooled and poured into water. The mixture was heated on the water-bath until the benzene had evaporated. The tarry mass which remained at the bottom of the beaker was found to be insoluble in benzene, alcohol, ether, chloroform, and acids. It did not, therefore, lend itself to further investigation.

Lack of material prevented the carrying out of any more experiments of this kind.

In the Friedel and Crafts reaction every new substance seems to require different conditions, which must be determined experimentally for each case. And for this reason the result of the above single experiment cannot be considered conclusive as to whether the reaction expressed by the equation,



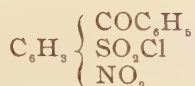
may not take place under certain conditions.

Comparison of Paranitroorthophenylsulphonebenzoyl Chloride with Paranitroorthobenzoylbenzenesulphone Chloride.

The compound obtained by Hollis¹ from the action of benzene and aluminum chloride on the isomeric chlorides of paranitroorthosulphobenzoic acid, crystallizes from its solution in benzene in the form of purple or green monoclinic crystals, melting at 177° C. It yields a non-crystallizable acid when boiled with water, and when treated with ammonia it combines with it, with the loss of hydrochloric acid and water, to form a lactim which melts at 234° C., and which is not very soluble in alcohol. Its reactions, therefore, are in accordance

¹ *Loc. cit.*

with what we should expect from a compound having the formula



Paranitroorthophenylsulphonebenzoyl chloride, isomeric with the above compound, crystallizes from benzene in colorless or light yellow, rhombic crystals melting at 109°C . It forms a well crystallized acid when boiled with water, which melts at 196°C .; and it reacts with ammonia to form an amide crystallizing in prisms which melt at 191° to 192°C ., and are readily soluble in alcohol. These properties characterize it as quite distinct from the compound of the same empirical composition described above.

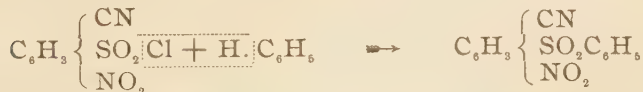
AN ATTEMPT TO TRANSFORM PARANITROORTHOCYANBENZENESULPHONIC ACID INTO PARANITROORTHOPHENYLSULPHONEBENZOIC ACID.

The unsymmetrical chloride of paranitroorthosulphobenzoic acid is converted into the ammonium salt of paranitroorthocyanbenzenesulphonic acid, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CN} \\ \text{SO}_2\text{ONH}_4 \\ \text{NO}_2 \end{array} \right.$, when treated with

a solution of ammonia. It was thought that this substance might furnish the starting point for another method for the preparation of paranitroorthophenylsulphonebenzoic acid. By the action of phosphorus pentachloride on the potassium salt of this acid, paranitroorthocyanbenzenesulphone chloride,

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CN} \\ \text{SO}_2\text{Cl} \\ \text{NO}_2 \end{array} \right.$, is formed.¹ It was hoped that by the action of

benzene and aluminum chloride this would yield paranitroorthocyanidiphenylsulphone according to the reaction,



which by hydrolysis of the cyan residue would give paranitroorthophenylsulphonebenzoic acid,

¹ Remsen and Gray : Am. Chem. J., 19, 510.



The material for the experiments was prepared by Mr. W. E. Henderson, of this laboratory. The ammonium salt, which was obtained as a waste-product in the preparation of the symmetrical chloride of paranitroorthosulphobenzoic acid, was converted into the potassium salt by adding caustic potash or potassium chloride to its solution in hot water. The potassium salt is difficultly soluble in cold water, and separates out as the solution cools in the form of needles. Potassium chloride was found to work more satisfactorily than potassium hydrate. An analysis by Mr. Henderson of the potassium salt prepared in this way confirmed its purity. The salt was heated two or three hours in an air-bath at about 130° C. to free it from water of crystallization.

Twenty-five grams of the dry potassium salt were mixed in a mortar with an equal weight of phosphorus pentachloride, placed in an evaporating dish, and heated to 140° C. on a sulphuric-acid bath. After the reaction had ceased, the heating was continued half an hour longer, to evaporate off the phosphorus oxychloride. It was allowed to cool to the ordinary temperature and treated with cold water, which caused it to solidify. It was ground to a fine powder, washed several times with water, drained, and dissolved in chloroform. A small portion remained undissolved, which was probably the anhydride of the acid. Some of the acid was also recovered from the water used in washing the chloride, showing that the use of a larger quantity of phosphorus pentachloride is necessary to convert all of the potassium salt into the chloride. The chloroform solution was freed from water with calcium chloride, and allowed to evaporate spontaneously. Large, well-formed, quadrilateral prismatic crystals were obtained, which melted at 104°.5–105°.5 C. (uncor.).

Ten grams of the chloride were dissolved in an equal weight of warm benzene, in a flask provided with a condensing-tube, and eight grams of powdered aluminum chloride added gradually, in small portions at a time. No reaction took place until the solution was warmed. A brown, tarry

mass then collected at the bottom of the flask, forming a solid cake with the aluminum chloride. The solution was heated on the water-bath until hydrochloric acid was no longer given off. Although considerable hydrochloric acid was liberated, there was no apparent evolution from the surface of the aluminum chloride, as is usually the case in the Friedel and Crafts reaction. The benzene solution, which had a slight brown color, was poured into water, and the mixture heated on the water-bath until the benzene had all evaporated. Nothing remained in the water but a small amount of undecomposed chloride. The residue in the flask was washed with dilute hydrochloric acid and extracted with alcohol. That which remained undissolved in the alcohol was a brown, amorphous powder, insoluble in ether, benzene, chloroform and concentrated acids. The alcoholic extract was evaporated to dryness on the water-bath, leaving a brown, tarry mass, from which no crystalline product could be obtained. It was dissolved in ether, chloroform, benzene and acetone, but separated out in the same form on evaporation of the solutions.

The experiment was repeated, using 100 cc. of benzene to ten grams of the chloride, and the result was essentially the same.

The presence of the cyan group probably interferes with the action of benzene on the sulphone chloride residue.

Conclusions.

The results of this investigation lead to the following conclusions:

1. Paranitroorthotolylphenylsulphone can be readily obtained by the action of benzene and aluminum chloride on paranitroorthotoluenesulphone chloride.

2. This sulphone has the general properties of aromatic sulphones, and certain other properties due to the presence of the nitro group.

3. Paranitroorthotolylphenylsulphone is oxidized by potassium permanganate in neutral solution to paranitroorthophenylsulphonebenzoic acid. And this acid is quite different in properties from the isomeric compound obtained by decomposing with water, the product of the action of benzene and

aluminum chloride on the chlorides of paranitroorthosulphobenzoic acid.

4. Paranitroorthophenylsulphonebenzoic acid passes over quantitatively into paranitroorthophenylsulphonebenzoyl chloride when treated with phosphorus pentachloride.

5. Paranitroorthophenylsulphonebenzoyl chloride has perfectly definite properties, which distinguish it from the isomeric compound obtained by the action of benzene and aluminum chloride on the chlorides of paranitroorthosulphobenzoic acid, especially the formation of an amide by the action of ammonia, while the latter forms a lactim.

BIOGRAPHICAL.

Robert Stewart Norris was born in Belleville, Wis., January 19, 1869. He received his primary education in the public schools of Topeka, Kansas, and prepared for college in the academic department of Washburn College at the same place. In 1887 he removed to Los Angeles, California, and entered the University of California in 1888, graduating in 1892 with the degree of Bachelor of Science. He remained at the same institution as assistant in chemistry for three years, and entered Johns Hopkins University in 1895, where he has since pursued courses in chemistry, general biology, and physiology. He was appointed University Scholar during the present year.

BALTIMORE, May, 1897.



